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REMOVAL OF CARBON MONOXIDE - PHYSICAL
ADSORPTION ON NATURAL AND SYNTHETIC
ZEOLITES

Francesco Alfani, Guido Grecq, Jr. and
Gabriele Iorio

Translation of "Abbatimento di ossido di carbonio -
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REMOVAL OF CARBON MONOXIDE.
PHYSICAL ADSORPTION ON
NATURAL AND SYNTHETIC ZEOLITES.

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The main purpose of the investigations the results of which are described in this article is that of verifying the possibility of using natural zeolite materials in the elimination of polluting gases. In particular, attention is focused on pollution with carbon monoxide, whose concentration may reach dangerous levels in places such as vehicle tunnels, underground parking lots, etc. The elimination of carbon monoxide is also of interest in some industrial processes relating to the production of pure gases.

As regards more directly the problems of atmospheric pollution, the technique most widely used up to now is based on the effect of ventilation plants.

In the more specific area of the environmental conditioning of vehicle tunnels, where the use of axial accelerators is constant, there are limits of application deriving from the fact that it is impossible to exceed maximum values in the speed of the air, due to problems of safety in case of fire and at the costs of plant and management [1].

Consequently, for the purpose of improving the control of atmospheric pollution it is necessary to use techniques of "in situ"

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removal, such as, for instance, selective adsorption on suitable adsorption beds.

The choice of these materials is obviously prompted by economic considerations related to their costs and their adsorption properties.

In this article, attention is drawn particularly to the physical adsorption of carbon monoxide on natural tufas, abundantly available in the countryside and therefore characterized by low cost.

The adsorption characteristics of these materials were compared with those of synthetic molecular sieves, characterized obviously by much higher costs. The experimental tests were carried out with recourse to a dynamic technique described elsewhere.

Adsorption Materials

The specimens of natural tufas used in the investigation come from caves located in the province of Avellino. The content of zeolite fraction (cabasite) is about 65% weight and the weighted chemical composition, determined in conditions of saturation (environmental humidity, 54.5%), is given in Table 1 [3].

Table 1: Weighted chemical composition of cabasitic tufa.

SiO ₂	50,62
Al ₂ O ₃	16,05
Fe ₂ O ₃	3,75
FeO	0,35
TiO ₂	0,46
MnO	0,11
P ₂ O ₅	0,15
CaO	4,29
MgO	1,33
Na ₂ O	2,55
K ₂ O	7,02
H ₂ O	13,32

Before they are used, the tufa specimens are ground and sifted; the adsorption tests were accomplished on the fraction between 10 and 20 mesh.

The comparison tests were conducted on the following synthetic zeolites (BDH):

- 3 A (1/8" cylindrical pellets)
- 4 A (4-8 mesh spherical pellets)
- 5 A (1/8" cylindrical pellets)
- 13 X (1/16" cylindrical pellets).

Wherever the possible presence of external resistance to the transport of matter was determined, some tests were carried out initially using both tufas and molecular sieves in the form of powder. The results of these preliminary tests show clearly that the external resistances are negligible. Since all the materials used show a high absorption capacity as compared with the water vapor, they were pre-treated in a current of He for 12 hours at 250°C.

In the adsorption tests, gaseous mixtures were used pre-constituted of He/CO (SiO) with the following volumetric compositions: 0.97%; 10.31%; 19.70%.

The choice of helium as transport gas was imposed by the adoption of a detector with thermal conductivity [2].

Experimental Technique

The technique used to determine the isotherms of adsorption was described in detail in [2]. In its general form, it consists in the analysis of the transient response of a column filled with

the adsorbing material and stressed with a step of known amplitude in the concentration of carbon monoxide. The adsorbing column is maintained initially in a flow of He. At the time $t = 0$, the step of amplitude c^0 of CO is sent obtaining a response in 52 terms of the concentration of the effluent CO as shown in Fig. 1.

The signal remains at the value corresponding to pure He for a time equal to τ_2 which indicates the complete adsorption of CO. "Subsequently the latter reaches quickly the final value corresponding to a concentration of CO equal to c^0 (feed value) indicating thus that there is saturation of the adsorbing bed. The interval $0-\tau_1$ (see Fig. 1) corresponds to the delay induced by the connections between the column and the measurement element. Therefore only the area $(\tau_2-\tau_1) c^0$ is connected to the amount of CO adsorbed.

The form of the response curves, which is independent of the partial pressures of CO in gaseous phase and the velocity of flow, indicates that the transport of matter inside the single adsorbing grain occurs with negligible resistance and the adsorption kinetics are fast.

As regards the measurement element used, it is proper to emphasize the considerable sensitivity which made it possible in the experimental conditions adopted to measure a minimum amount of CO adsorbed equal to 10^{-6} gmoles/g adsorber. This made it possible to determine the adsorbing capacities up to a temperature of 350°C with a partial CO pressure of 0.5 atm.

Fig. 2 shows a flow diagram of the experimental equipment used.

Discussion of the Results

Figs. 3, 4 and 5 give the adsorption isotherm of carbon monoxide

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on tufa and 5A and 13 X zeolites in terms of gmoles of CO adsorbed per gram of adsorber against the

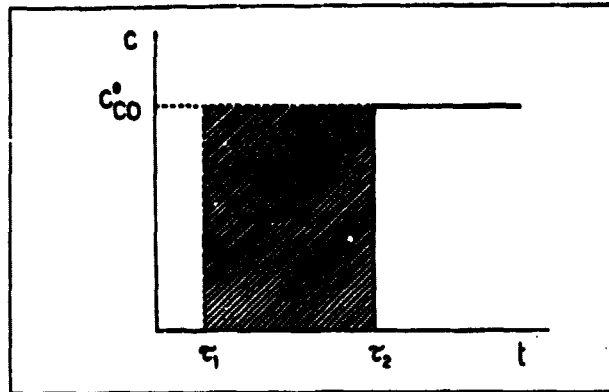


Fig. 1 Step response of the adsorbing column: concentration of CO in gaseous phase over time.

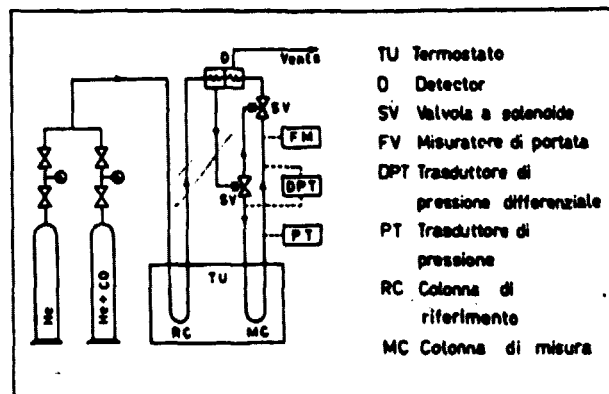


Fig. 2 Flow diagram of the equipment TU thermostat; D detector; SV solenoid valve; FV range gauge; DPT transducers of differential pressure; PT pressure transducer; RC reference column; MC measurement column.

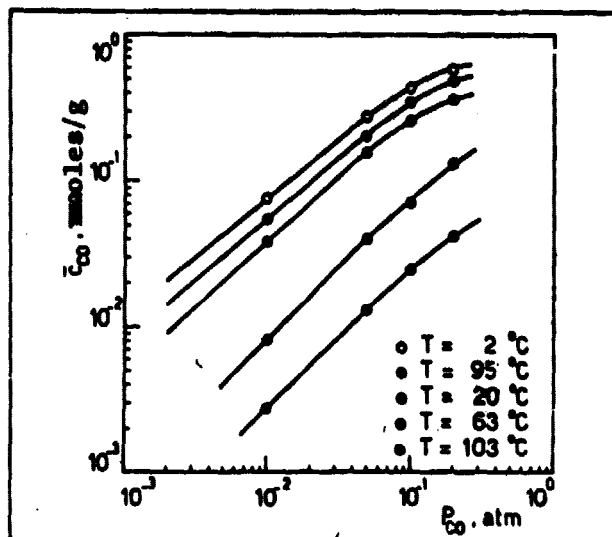


Fig. 3 Isotherms of adsorption of CO on tufa.

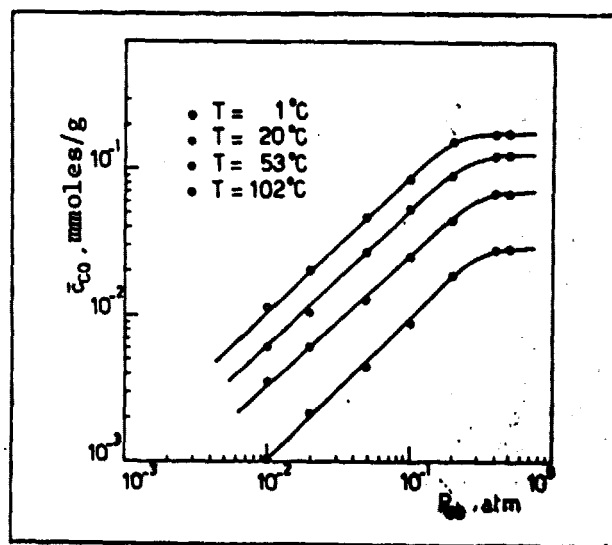


Fig. 4: Isotherms of adsorption of CO on 5 A zeolite.

partial pressure of CO in gaseous phase. An analysis of the results shows that the adsorption capacity of the tufa is approximately in the ratio of 1:5 and 1:2 with regard to that of the 5A and 13X zeolites, respectively, in the entire range of temperatures and par-

tial pressures of CO explored.

These results are justified on the basis of the indications given in [16], according to which the concentrations of active cations in the physical adsorption are 7.1, 3.8, 5.7, 2.9 moles/g for zeolites of type A, cabasites and 13 X, respectively.

But we must take into account the fact that the specimens of natural tufa used in the present study contain only about 65% in the zeolite fraction.

On the other hand, some initial tests conducted on zeolites of type 4A and 3A at ambiental temperature and partial CO pressure of 0.2 atm indicated that the amount of CO adsorbed is practically nil. This behavior which is quite different from the tufa and zeolites 5A and 13 X, on one hand, and 3A and 4A zeolites, on the other, with regard to the physical adsorption of CO may be attributed /53 to the different chemical composition and the different structural characteristics of the materials used. Actually the actual diameter of the pores [5] is equal to 4.1 Å for zeolites of the type Linde A and 7.4 Å for faujasite (13 X) and 3.7-4.2 Å for cabasite. Therefore, the average molecular dimensions of CO being 2.8 Å, there should be no steric obstacles to the penetration of the CO molecule in any of the adsorbing materials studied. But as regards the chemical composition of the zeolites, it should be noted that those of the type Linde A are prepared by inserting, by ion exchange in the initial porous structure, Ca^{++} cations in the 5A, Na^+ in the 4A and K^+ in the 3A. The average ionic radius of such cations increases in the order indicated; moreover with regard to the balance of charges, the concentration of the Ca^{++} ions in the 5A is half of that of the Na^+ and K^+ in 4A. and 3A. It is therefore plausible that the ion exchange with ions of sodium and potassium reduces considerably the initial diameter of the pores, thus causing the total disappearance of the adsorbing properties of the zeolites 4A and

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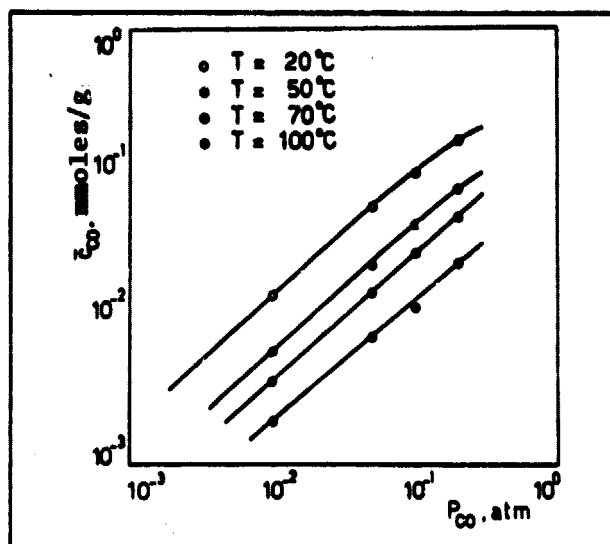


Fig. 5 Isotherms of adsorption of CO on 13 X zeolite.

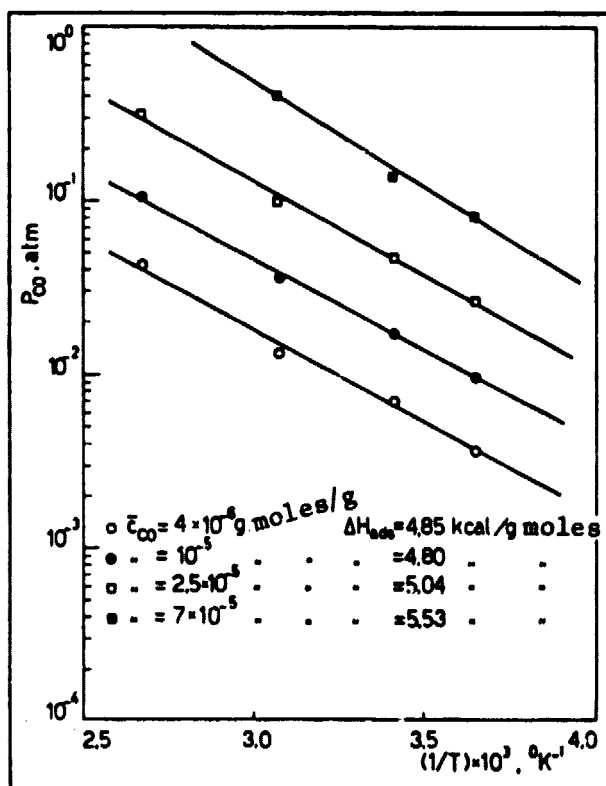


Fig. 6 Partial pressure of CO over $1/T$ for adsorption of CO on tufa with constant values of concentration of the adsorbate.

3A with regard to the molecule of CO. The results obtained in the present study, insofar as they concern the zeolites of the Linde A type, are consistent with what is observed in [6] in which it is emphasized how a zeolite A in the calcic form shows adsorption properties superior by far to those of the same zeolite in the sodic form.

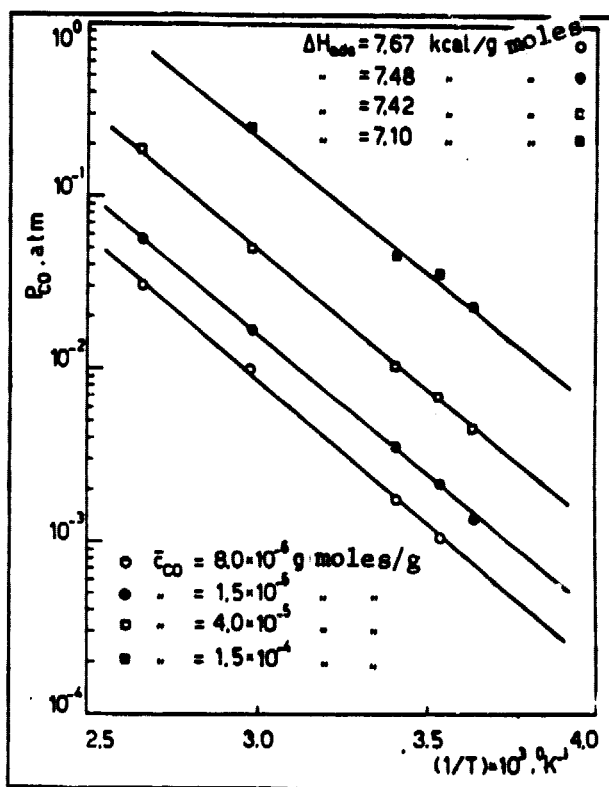


Figure 7: Partial pressure of CO over $1/T$ for the adsorption of CO on 5A zeolite with constant values of the concentrations of the adsorbate.

The experimental properties have made it possible to evaluate the isosteric heats of adsorption. Figs. 6, 7, and 8

show the curves of partial pressure of CO in the gaseous form over the inverse of the absolute temperature in accordance to different amounts of CO adsorbed. The data show high consistency with relation [7,8]:

$$\left[\frac{O \ln P_n}{O (1/T)} \right]_{\epsilon, A} = - \frac{\Delta H_{ads}}{R}$$

In conformance with data in the literature [13, 14, 15] the isotheric heat of adsorption proves to depend on the amount of adsorbate and on the type of cation occurring in the zeolite structure [10]. The dependence of ΔH of adsorption on the concentration of CO adsorbed is plotted in Fig. 9 for tufa. Under the experimental conditions adopted in this study, the values of ΔH_{ads} vary between 4.80 and 5.53 kcal/gmole for tufa, and between 7.10 and 7.67 for 13 X zeolite. These values are not unlike those indicated in [9], where a value was indicated of ΔH_{ads} equal to 6.9 Kcal/gmole for the adsorption of CO on NaX. /54

The increase of ΔH_{ads} with the increase of the concentration of the CO adsorbed indicates that the forces of interaction of adsorbate to adsorbate are dominant with regard to the forces of adsorbate-adsorber dispersion just as is expected for the adsorption of relatively small linear molecules such as those of CO on zeolites [16]. The adsorption tests conducted on tufa show that, with the increase of the partial pressure of CO, the amount adsorbed at different temperatures (see Fig. 3) tends to an asymptomatic value which may be expressed as a function of the temperature, by the relation:

$$\bar{r}^*(T) = \bar{r}^*(T_0) \exp [-\alpha (T - T_0)]$$

in which α is equal to $0.0174^\circ K^{-1}$. This behavior was attributed

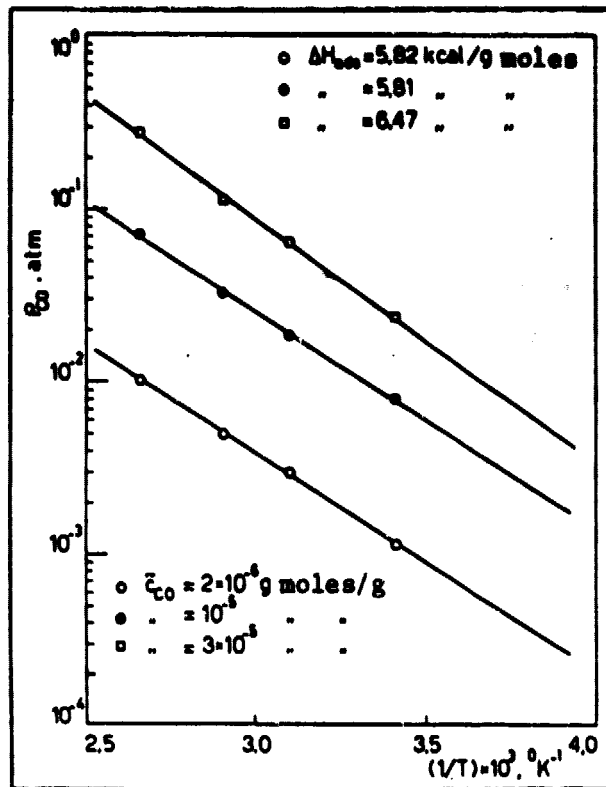


Fig. 8: Partial pressure of CO against $1/T$ for adsorption of CO on 13 X zeolite with constant values of the concentration of adsorbate.

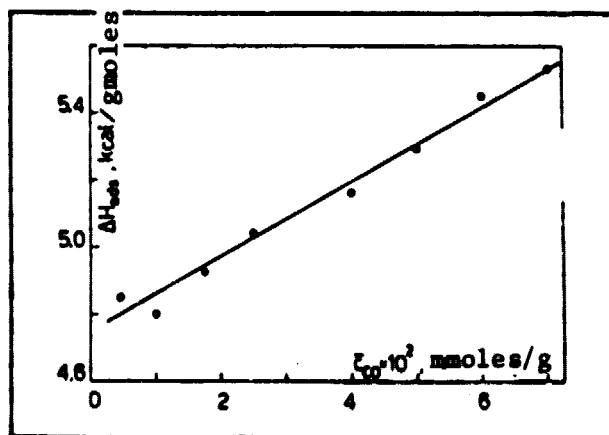


Fig. 9: Dependence of the isosteric heat of adsorption of CO on tufa on the amount adsorbed.

[11, 12, 13] to the filling of the volumes of the microporous structure of the zeolite. Actually a thermodynamic analysis conducted on this adsorption model allows the theoretical determination of the above indicated relation between the degree of filling of the microporous volume and the temperature, which involves the thermal coefficient α of limiting adsorption which is practically constant for a broad range of temperatures.

Conclusions

The linear variation of the adsorption isotherms, in accordance with the lower values of the partial pressure of CO explored, makes it possible to foresee the value of the amount of carbon monoxide adsorbed at the level of its maximum permissible concentration. The results of the adsorption tests carried out both on commercial zeolites and on tufa show how the adsorption capacity is rather limited in every case.

It is found that a direct application of the technique of elimination by physical adsorption of CO on systems of considerable potentials is difficult to implement. In any case, the adsorption properties of synthetic zeolites can be increased considerably [4] by means of ionic exchange which permits the substitution of the ions K^+ , Na^+ , Ca^{++} with ions of iron, cobalt and nickel able to form chemical bonds with the carbon monoxide.

In this respect an interesting characteristic of the country tufas is that of containing in their structure iron oxides which, after being reduced to metallic iron, could increase considerably the adsorption powers. In any case, even for the natural zeolites occurring in the tufa, it is possible to adopt ion exchange techniques identical to those used for synthetic zeolites for inserting in the lattice the ion species needed.

Experimental tests along these lines are now in progress.

Acknowledgments

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Symbols

A = weight of adsorption bed	g
c = concentration in gaseous phase	gmoles/cm ³
\bar{c} = concentration in adsorbate phase	gmoles/g
\bar{c}^* = limiting concentration of adsorbate	gmoles/g
p = partial pressure	atm
R = universal gas constant	cal/gmol ^o K
t = time	min
T = temperature	^o K
T ₀ = reference temperature	^o K

Greek symbols

ΔH_{ads}	= thermal coefficient	^o K-l
α	= isosteric adsorption head	Kcal/gmole
τ_1	= transport delay	min
τ_2	= duration of step response	min

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